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INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 15683 TpCm		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/GB 03/02682	International filing date (day/month/year) 23.06.2003	Priority date (day/month/year) 19.07.2002	
International Patent Classification (IPC) or both national classification and IPC C08J5/22			
Applicant AEA TECHNOLOGY BATTERY SYSTEMS LIMITED et al			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 5 sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the opinion</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input type="checkbox"/> Certain documents cited</p> <p>VII <input type="checkbox"/> Certain defects in the international application</p> <p>VIII <input type="checkbox"/> Certain observations on the international application</p>			
Date of submission of the demand 27.12.2003		Date of completion of this report 12.07.2004	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized Officer Lartigue, M-L Telephone No. +49 89 2399-8230 	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/GB 03/02682**

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1, 3, 4, 7-15	as originally filed
2, 5-6	filed with telefax on 07.06.2004

Claims, Numbers

1-11	filed with telefax on 07.06.2004
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2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-11
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-11
Industrial applicability (IA)	Yes: Claims	1-11
	No: Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB 03/02682

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

Reference is made to the following document: GB 2 309 701 (D1)

NOVELTY (Art. 33(2) PCT) and INVENTIVE STEP (Art. 33(3) PCT):

D1 discloses a process to produce porous polymeric membranes suitable for use in electrochemical cells. Said membranes are produced from polymers comprising vinylidene fluoride as defined in the present application (see D1 from page 2, line 15 to page 3, line 22). More particularly, Example 3 (see D1, page 11) discloses a process comprising:

- dispersing polyvinylidene fluoride (PVdF) or PVdF grafted with acrylic acid in a small volume of methanol (a non-solvent);
 - adding dimethyl acetamide (solvent) to dissolve the PVdF;
 - stirring and heating the solution;
 - casting the resulting slurry to form a thin layer;
 - drying the thin layer to evaporate the non-solvent and solvent and to obtain a membrane.
- Said Example 3 also discloses the fabrication of a laminate.

Hence, the process as defined in the present claims differs from D1, Example 3, in that

- 1) the boiling point of the non-solvent is higher than that of the solvent;
- 2) it specifies the temperature above which the PVdF solution is heated.

Consequently, the subject-matter of the present claims is novel over D1.

However, the subject-matter of the present claims does not involve an inventive step over D1 for the following reasons:

- the fact that D1, example 3 does not specified that the PVdF solution is heated above 40°C is not a significant difference because the aim of the heating step is, in both the present process and in D1, the dissolution of the PVdF and it is achieved in both the present process and in D1;
- it is not clear from the present application whether any effect results from the boiling point of the non-solvent being higher than that of the solvent. Hence, no technical problem seems to be solved by the present application over D1.

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polymeric electrolyte composition can be enhanced by grafting suitable mono-unsaturated groups onto the polymer chain, and in this case the polymeric chain might be a homopolymer PVdF, or a copolymer or terpolymer consisting primarily of vinylidene fluoride. It is also possible to make a solid polymer electrolyte by first making a porous film of the polymer material, and then immersing the film in the solution of lithium salt in an organic solvent so the electrolyte solution combines with the polymer film, as described in EP 0 730 316 A (Elf Atochem). However, with known methods of making porous membranes, it is difficult to achieve micropores of a substantially uniform size and to control the porosity of the resulting film.

Fuel cells use a porous membrane to separate the anode and the cathode. The membrane is typically a multilayered assembly and may include, for example, a porous membrane and one or more diffusion layers. Improved membranes are needed to improve the uniform delivery of gas to the fuel cell plate.

The present invention provides a process for producing a porous polymeric membrane which process comprises:

a) preparing a solution comprising a polymer which comprises vinylidene fluoride in a solvent /non-solvent mixture by dispersing the polymer in the non-solvent prior to addition of the solvent wherein the boiling point of the non-solvent is higher than that of the solvent;

b) holding the solution at an elevated temperature of at least 40°C until the polymer is completely solvated;

c) casting the solution to form a thin layer; and

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does not give reproducible membranes.

The non-solvent is a liquid which does not dissolve the polymer when used alone. The non-solvent should not
5 only dissolve in the solvent, but it should be miscible with the solvent in substantially all proportions. The boiling point of the non-solvent is higher than that of the solvent, preferably 20°C higher, more preferably 40°C higher or more. Examples of the non-solvents include
10 alcohols containing 6 to 20 carbon atoms such as, octanol, decanol and dodecanol, and mixtures thereof, preferably decanol, dodecanol and mixtures thereof. Particularly preferred non-solvents are a 50:50 mixture of dodecanol and decanol or dodecanol alone.

15 The solvent is a liquid which can dissolve or swell the polymer. The solvent may be chosen from for example ketones, ethers, N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), N,N-diethylacetamide, N-methyl-
20 2-pyrrolidone (NMP), hexamethylphosphoramide, tetramethylurea and dimethyl sulfoxide (DMSO) or a mixture thereof. DMF and NMP are preferred solvents. More preferably NMP is the solvent.

25 The ratio of non-solvent to solvent in the solution can be varied. Typically the proportion of non-solvent in the solvent/non-solvent mixture is 2 to 30 wt %, preferably 5 to 15 wt %, more preferably 7 to 10 wt%.

30 The amount of polymer in the solution is generally from 3 to 30 wt %, preferably from 5 to 20 wt %, more preferably from 8 to 15 wt %.

35 Solvation of the polymer takes place at an elevated temperature. An elevated temperature is a temperature above room temperature (which is taken to be 20°C). The

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temperature chosen is specific to the polymer and solvent/non-solvent combination that is used and the amount of time over which solvation takes place. The elevated temperature is at least 40°C, more typically at least 50°C for example 55°C. A lower temperature may be used if solvation takes place over a longer period of time.

Typically solvation takes place over several days.

10 The solvation process continues until the polymer(s) are completely solvated. The exact solvation time required varies depending on the solvent/non-solvent mixture, the choice of polymer or polymers and the temperature used. Typically solvation takes place over from 4 to 14 days,

15 preferably 5 to 10 days and most preferably 5 to 7 days. For example, PVdF (Solvay Solef 6020/1001) in N-methyl-2-pyrrolidone and a 50:50 mixture of decanol and dodecanol typically solvates completely in from 5 to 14 days, typically 10 days depending on the ratio of non-solvent

20 to solvent in the solution. Gel formation during the solvation process is so slow as to be negligible. Solvation also occurs without the formation of a microgel.

25 Once the polymer is fully solvated, the solution is stable at room temperature for several weeks. Thus, the viscosity of the solution does not change over time, the colour of the solution remains constant and there is no separation of the solvent or non-solvent from the

30 solution. Furthermore the solution forms reproducible membranes with consistent properties, when cast. Therefore it is not necessary to cast the solution into a film immediately.

35 The solution is typically cast onto a non-porous substrate such as aluminium foil or Mylar film. The

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Claims

1. A process for producing a porous polymeric membrane which process comprises:

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a) preparing a solution comprising a polymer which comprises vinylidene fluoride in a solvent/non-solvent mixture by dispersing the polymer in the non-solvent prior to addition of the solvent wherein the boiling point of the non-solvent is higher than that of the solvent;

10

b) holding the solution at an elevated temperature of at least 40°C until the polymer is completely solvated;

15

c) casting the solution to form a thin layer; and

d) drying the thin layer to form a membrane.

20

2. Process according to claim 1 wherein the solution comprises polyvinylidene fluoride (PVdF).

3. Process according to claim 1 or 2 wherein the solvent is N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA) or N-methyl-2-pyrrolidone (NMP).

25

4. Process according to any of the preceding claims wherein the non-solvent is octanol, decanol, dodecanol or a mixture thereof.

30

5. Process according to any of the preceding claims wherein the solution is solvated for up to 14 days.

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6. Process according to any of the preceding claims wherein mono-unsaturated carboxylic, sulphonic or phosphonic acid, ester or amide groups are grafted onto the vinylidene fluoride.

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7. A membrane produced by the process according to any of the preceding claims.

8. A laminate comprising a membrane produced according to the process of any of claims 1 to 6.

9. Use of a membrane produced according to the process of any of claims 1 to 5 or a membrane according to any of claims 7 to 9 in a battery.

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10. Use of a membrane produced according to the process of any of claims 1 to 6 in a fuel cell.

11. Use of a laminate according to claim 8 in a fuel cell.

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